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THE SPECTROSCOPY AND REACTION KINETICS OF COORDINATED
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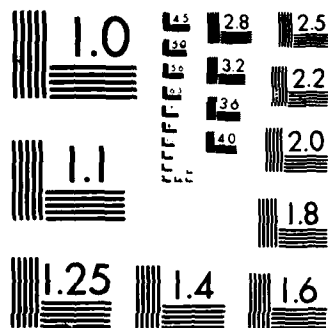
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The Spectroscopy and Reaction Kinetics of
Coordinated Unsaturated Metal Carbonyls

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Coordinatively unsaturated metals are important chemical species with a variety of interesting and unique chemical properties. These species have been shown to be exceedingly reactive. They are important catalysts, reaction intermediates and can form oligomers and metal clusters containing multiple metal centers.¹ Despite their importance and a great deal of interest in this area, little is known regarding details of the structure or reactivity of coordinatively unsaturated metals. Their extreme reactivity has heretofore been an impediment to detailed study of these species in the liquid phase and has virtually precluded study in the gas phase. Until recently nothing was known about the mechanism or kinetics for reactions or cluster formation in these systems.

In an effort to alter that situation we developed an apparatus and a technique which allows us to study coordinatively unsaturated metals in either phase in real time. The use of transient absorption spectroscopy has allowed us to detect and monitor coordinatively unsaturated metals. Most of our studies to date have involved excimer laser photolysis of volatile metal carbonyls to yield gas phase coordinatively unsaturated metal carbonyls or metal atoms. Most of our work has employed an apparatus that uses a line tunable CO laser, as a probe, to monitor the change in absorption of the sample following the excimer laser photolysis pulse. However, we have now integrated

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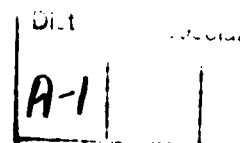
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a cw diode laser into the apparatus. This allows us to probe transient species in any region of the infrared and thus vastly increase the versatility of the apparatus.

To actually generate a transient spectrum the change in absorption of the probe laser is monitored at a variety of different laser frequencies with the time versus absorbance signal digitized via a transient digitizer which feeds the data to a signal averager from which it is fed to a computer. The computer takes all the frequency dependent data and assembles it into a transient absorption spectrum which can be displayed as a function of time following the photolysis pulse. Once features in the transient absorption spectrum are identified, a specific feature can be monitored as a function of time and its kinetic behavior discerned. Our current apparatus has a time response of 30 nsec, a frequency range of 350-2350 and 2900-3300 cm^{-1} , and a typical detection sensitivity corresponding to 10^9 coordinatively unsaturated metal carbonyl molecules.

With the above technique, we have been able to obtain the first gas phase infrared spectrum of a coordinatively unsaturated metal.² We have obtained infrared spectra in the CO stretch region for the species $\text{Fe}(\text{CO})_x$ ($x = 2, 3, 4$) and have measured the rate of reaction of $\text{Fe}(\text{CO})_x$ with CO and the activation energies for these reactions.³ We have made the first real time observation of and are measuring the kinetics for clustering of $\text{Fe}(\text{CO})_x$ species.⁴ We have performed similar studies for the $\text{Cr}(\text{CO})_6$ system, obtaining spectra for $\text{Cr}(\text{CO})_x$ ($x = 2, 3, 4, 5$)^{5,6} and have measured rates of reactions of $\text{Cr}(\text{CO})_5$ with CO, CH_4 , N_2 , H_2 and C_6H_6 .⁷ We have also observed a heretofore unreported clustering process in the $\text{Cr}(\text{CO})_x$ system. We find that all the $\text{Cr}(\text{CO})_x$ fragments react readily with parent. In particular, we have investigated in detail the



clustering process for the reaction of $\text{Cr}(\text{CO})_4$ and $\text{Cr}(\text{CO})_5$ with parent. We find that both reactions occur at a rate that is within a factor of two of gas kinetics.⁶ We assign the species initially produced via these clustering reactions to $\text{Cr}_2(\text{CO})_{10}$ and $\text{Cr}_2(\text{CO})_{11}$, respectively, and have recorded the first gas phase spectra for these species in the carbonyl stretch region.⁶

We have also obtained results on the $\text{Mn}_2(\text{CO})_{10}$ system.^{8,9} As with $\text{Cr}(\text{CO})_6$ and $\text{Fe}(\text{CO})_5$, we have recorded the spectra of the photofragments identified following photolysis at 193, 249 and 351 nm.⁹ We have identified the major photoproducts and have measured the rate of reaction of $\text{Mn}_2(\text{CO})_9$ with CO and the rate of reaction of two $\text{Mn}(\text{CO})_5$ radicals to regenerate $\text{Mn}_2(\text{CO})_{10}$. Interestingly, the reaction of $\text{Mn}_2(\text{CO})_9$ with CO is quite slow and we are exploring the structural ramifications of this observation. The reaction of two $\text{Mn}(\text{CO})_5$ radicals is very rapid, almost gas kinetic, and represents the first measurement of the actual rate of formation of a metal-metal bond in the gas phase.

Most recently we have been investigating the clustering process in the $\text{Fe}(\text{CO})_5$ system in more detail.¹⁰ We find that only one of two isomers of $\text{Fe}_2(\text{CO})_8$ forms on reaction of $\text{Fe}(\text{CO})_3$ with $\text{Fe}(\text{CO})_5$. Furthermore, the isomer that is produced in the gas phase has been observed to be the less stable isomer in the matrix. We believe this situation occurs because the kinetics of reaction of $\text{Fe}(\text{CO})_3$ with $\text{Fe}(\text{CO})_5$ is spin controlled and the isomer we observed in the gas phase, the bridged form of $\text{Fe}_2(\text{CO})_8$, is a triplet while the unbridged form of $\text{Fe}_2(\text{CO})_8$ is a singlet. We are working to verify this hypothesis which could have important ramifications for understanding and predicting which clustering reactions will occur in the gas phase.

We are also investigating the $\text{Fe}(\text{CO})_2(\text{NO})_2$ system where we are primarily interested in determining the relative importance of simple addition reactions versus displacement reactions.¹¹ We are probing this question by looking at reactions that occur following photolysis of $\text{Fe}(\text{CO})_5$ in a bath of NO molecules. Since $\text{Fe}(\text{CO})_2(\text{NO})_2$ is the only stable iron carbonyl nitrosyl we are investigating how the kinetics and branching ratios for reaction of the various $\text{Fe}(\text{CO})_x$ moieties lead to this species.

Finally, we are investigating some predictions on relative rates of reaction of metal carbonyls with various ligands which were made by Roald Hoffmann based on an inorganic analog of Woodward-Hoffmann orbital symmetry rules.¹² Specifically we are looking at the reaction of conjugated versus unconjugated dienes with $\text{Fe}(\text{CO})_3$ and $\text{Cr}(\text{CO})_4$.¹³ Hoffmann predicted that the former species should react with conjugated dienes faster than with unconjugated dienes and that the latter species should behave in an opposite fashion. These predictions have never been tested because of the prior inability of experimentalists to produce specific coordinatively unsaturated metal carbonyls in a controlled fashion in the gas phase. Obviously these rules for reaction, which have been so important in the understanding of organic reaction kinetics, could also be of paramount importance in predicting rates and pathways of reactions of organometallic species.

The above work has also allowed us to formulate a hypothesis regarding the mechanism of photodissociation in these systems and provide us with insight into how to tailor the dissociation process to produce desired photoproducts. It also allows us to intelligently speculate on the timescale for dissociation.¹⁴

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- a) Detection of Transient Organometallic Species by Fast Time-Resolved IR Spectroscopy.
M. Poliakoff and E. Weitz
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- b) Gas Phase Infrared Spectroscopy and Recombination Kinetics for $\text{Mn}(\text{CO})_5$ Generated Via XeF Laser Photolysis of $\text{Mn}_2(\text{CO})_{10}$.
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- c) The Wavelength Dependence of Excimer Laser Photolysis of $\text{Cr}(\text{CO})_6$ in the Gas Phase. A Study of the Infrared Spectroscopy and Reactions of $\text{Cr}(\text{CO})_x$ ($x = 5, 4, 3, 2$) Fragments.
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- d) The Wavelength Dependence of Excimer Laser Photolysis of $\text{Fe}(\text{CO})_5$ in the Gas Phase: Transient Infrared Spectroscopy and Kinetics of $\text{Fe}(\text{CO})_x$ ($x = 4, 3, 2$) Photofragments.
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T. A. Seder - graduate student
S. Gravelle - graduate student
R. Ryther - graduate student
L. van der Burgt - postdoctoral research associate

Papers presented relating to project area 10/1/85-9/30/86

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